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Studies on the Stability of MF Resin Solutions: Investigations on Network Formation

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Summary: The phenomenon of thixotropy of melamine-formaldehyde (MF) resins has been investigated. A series of MF-resins with varying F/M ratios, different condensation times and pH during the condensation has been prepared. The storage stability at room temperature was measured using viscosimetry, polarization microscopy, NMR-spectroscopy and XRD. The visible changes observed in polarization microscopy (i. e. the formation of micron sized structures) correlate with the increase of viscosity related to the formation of thixotropy. The formation of a transient network can be concluded on basis of nmr-relaxation measurements and viscosimetry.

Introduction

Melamine Formaldehyde (MF) resins are among the most widely used industrial resins.[1] The final resin materials are usually prepared in two separated condensation steps. During the first step formaldehyde reacts with melamine in aqueous solution yielding a precondensate mixture of different monomeric as well as short linear and branched oligomeric melamine compounds. Among the factors which determine the composition the most prominent are the temperature and length of condensation, the pH of condensation as well as the order and time course of heating and reagent addition.[2] The obtained resin solutions are normally of low viscosity and colorless. Such MF solutions are cured in second stage by the application of heat, pressure or an acid catalyst to give an insoluble highly crosslinked resin.

An important factor with respect to the technical use of MF solutions relates to their long-term storage stability. Since these precondensates consist of approximately 60% solid content (oven measured), stable rheological properties are important. It is well known that the window of stability during the proceeding of the condensation reaction is very small and strongly related to the presence of monomeric and oligomeric structures (Figure 1). Thus, instable resins may show thixotropic behavior during storage at room temperature leading to a strong increase of viscosity, a shear induced

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loss of viscosity as well as a loss of transparency. Such solidified MF systems can be liquefied by mechanical stirring using high shear or warming to at least 30 – 40 °C. It has been proven that aged MF solutions remain chemically unchanged thus excluding chemical crosslinking or alteration due to condensation during room temperature storage. On the other hand the physical reason of the aging process is not well understood and may involve crystallization, physical gelation or liquid/liquid phase separation.

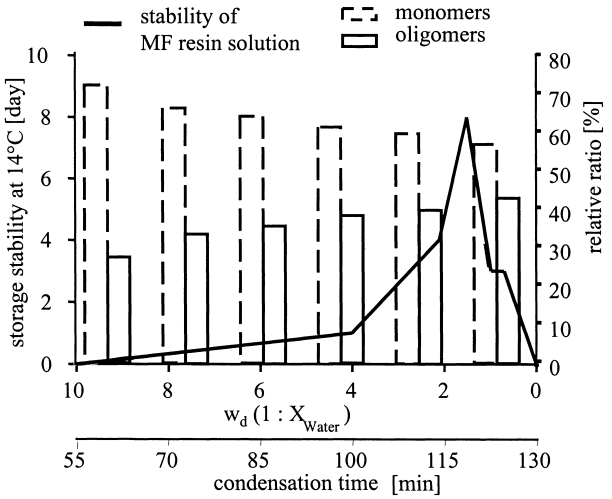

Figure 1. Storage stability and monomers to oligomers ratio of MF resin solutions depending on the water dilutability (w_d) and the condensation time.

Jahromi et. al.[3-5] have recently published evidence using resins with a solid content of about 50 %, that indicate a superposition of crystallization and phase separation effects. However since his resin compositions are far from the technically used materials (i.e. lower solids content) we were interested in a closer investigation of the phenomenon of thixotropy in technical MF resins. Those are also a good model system for other industrial important melamine containing resin materials such as MUF resins due to their lower degree of compositional complexity. Of particular interest was the nature of molecular interactions responsible for the increase in viscosity. Since thixotropy in polymeric systems can be often explained via the formation of particles and their aggregation and network formation processes[6,7] a similar model was searched for in the present MF resins. The approach was multivariant taking into account the various possible physical phenomena. Thus NMR-spectroscopy, X-ray diffraction, rheology and polarization light microscopy were used to probe the molecular dynamics and crystallization processes during the gelation process.

Experimental

Methods

^{1}H NMR experiments: The fresh MF resin solutions were diluted with 25 % D_2O and aged at 14°C directly in NMR tubes. The spectra were recorded with a Buker AMX 300 spectrometer. The standard inversion-recovery technique was used for spin-lattice relaxation times (T_1) measurements, whereas the Carr-Purcell-Meiboom-Gill (CPMG) multipulse sequence was employed for Spin-Spin relaxation times (T_2) determinations.

X-Ray diffraction measurements were performed with a powder diffractometer (X'Pert, Philips) using Cu-$K\alpha_{1,2}$-radiation Cu-$K\alpha_{1,2}$-radiation between 5° and 60° in 2θ (4h measuring time.

Optical microscopy: The optical pattern was examined with a Leitz Orthoplan microscope with the MF resin sample between crossed and decrossed polarizers. To aviod drying of the resin the samples were covered with silicone oil.

Rheology: Rheological measurements were carried out at a cone/plate rheometer (MCR 300, Physica) with a CP50-1 cone spindle (1.0° cone angle, 50mm cone radius). The distance cone-plate was adjusted at 50μm for all measurements.

Experimental Induction of Thixotropy

The solid content (SC) of the resin was adjusted to the (technically used) value of 60% (oven measured) leading to an increase of the effect of gelation in these materials. The final stability window investigated was adjusted to a water dilutability (w_d) of 1 : 1, which corresponds to the technically used area. In order to reproducibly generate resins of defined stability various parameters such as the F/M-ratio and the starting pH value were investigated (Figure 2).

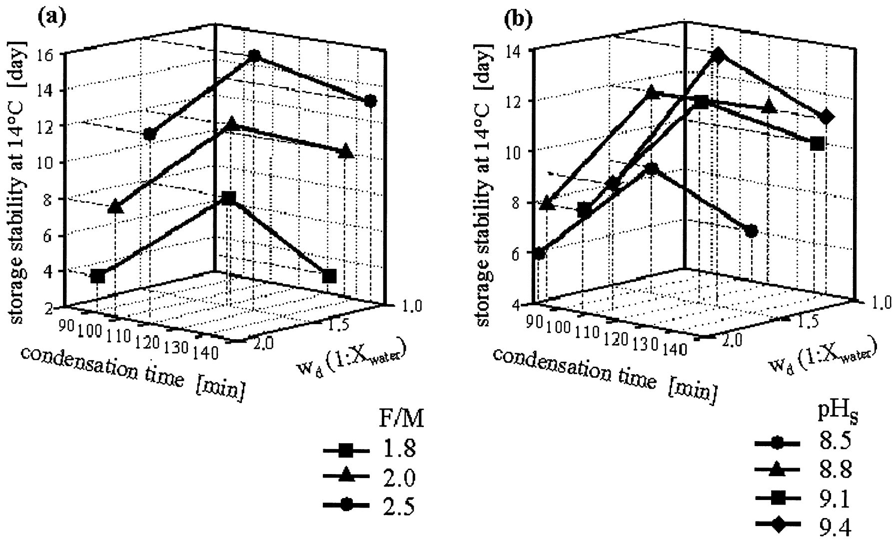

Figure 2. Storage stability in dependence of (a) the F/M ratio and (b) the starting pH-Value (pH_S) of condensation.

Additionally the heating time to reach the desired condensation temperature was varied in order to study behavior at extreme measurement points (Figure 3). The results clearly demonstrate a higher stability with increasing F/M-ratio, longer condensation times and more alkaline pH during condensation. Thus we were able by appropriate choice of parameters to effectively control the stability.

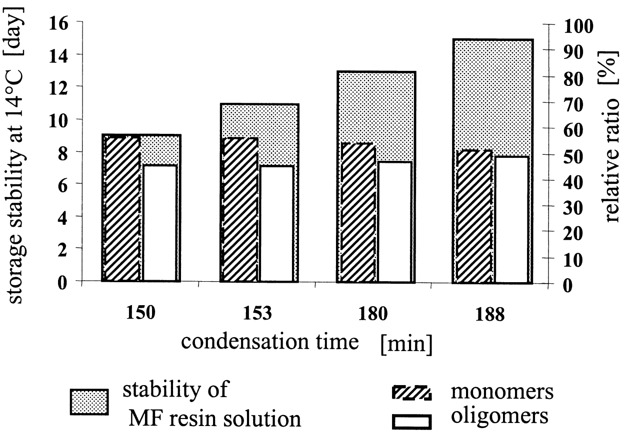

Figure 3. Storage stability and monomer/oligomer ratio in dependence of the condensation time.

However, in contrast to Jahromi et. al.[3] we were not able to separate the stable and instable parts of the resin materials by centrifugation processes, presumably due to their higher solids content. Thus we were not able to separately analyze the stable and instable fractions within the resin. Instead alternative analytical techniques such as polarization microscopy and NMR-spectroscopy were used to probe the gelation process.

Polarization Microscopy / XRD

Since the occurrence of instability is also governed by a visible loss of transparency we followed this process by polarized light microscopy. This method is able to detect particles down to the micrometer range in transparent and semitransparent samples[8]. Main changes were observed by use of this method. With increasing storage time the occurrence of micron sized, intransparent aggregates was observed, which after a longer time revealed an increased aggregation towards berry like structures (Figure 4a-d).

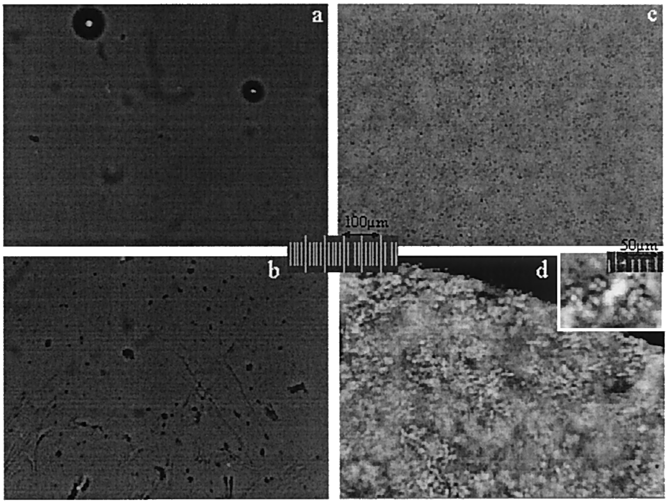

Figure 4. Polarization microscopy of resin solutions : (a) fresh resin with two air bubbles (b) 5 days aged (c) 15 days aged (d) 30 days aged.

The number of such aggregates within a berry was 4 to 6 indicating a close to hexagonal shaped arrangement. This process was absent in stable resins, which remained transparent throughout the storage time of stability. Additionally, XRD-measurements were performed to check for the formation of small sized microcrystallites. As seen in Figure 5 the absence of sharp transitions indicate the absence of crystalline material. On the other hand the appearance of a second weak amorphous signal in the x-ray data of aged samples indicated a higher structural order.

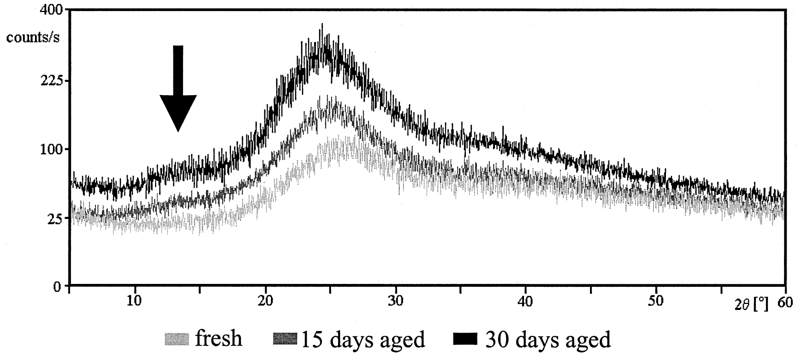

Figure 5. XRD of fresh and aged resins.

NMR-Spectroscopy

In order to probe the molecular mobility of the resins during the aging process we conducted extensive relaxation measurements using high resolution solid state NMR-spectroscopy at 300 MHz. This method represents a hybrid method between solid state NMR-spectroscopy and solution state NMR-spectroscopy yielding highly resolved spectra via magic angle spinning experiments. The native resins can be measured directly without the use of freeze drying steps and/or dilution methods. Results of T_1 and T_2 relaxation of the HDO resonance are shown in Table 1. Comparing thixotropic and fresh resins no change in T_1 could be observed. Due to the fact that T_1 is mainly affected by the fast, local motions in the MHz range of the molecular segments depending primarily on the free volume of molecules, it is unlikely that crystallization took place upon aging. Transverse Relaxation T_2 however indicated the splitting in two components within the aged resin, characterized with one long and one short relaxation constant, T_{2L} and T_{2S} respectively (Table 1).

Table 1. T_1 and T_2 relaxation of fresh and aged MF resin solutions respectively.

F/M	T_1 [ms]	
	fresh MF samples	aged MF samples
1.81	689	794
2.00	680	735
2.50	711	790

	T_2 [ms]		
F/M	fresh MF samples	aged MF samples	
		T_{2L}	T_{2S}
1.8	52	35	3.8
2.0	31	33	3.5
2.5	31	40	3.1

This indicates the presence of two states of water referred to as "free" and "bound" water respectively. The formation of network structures can thus be assumed, in which water resides in cavities (bound water) with a short T_{2S} component and water residing outside the cavities (free water) with a long T_{2L} relaxation time. Similar two component systems have been described in other gels on basis of noncovalent networks.[9-12]

Rheology

To figure out the type and strength of the network formation during the storage period, we have subjected the resin solutions to strain dependent rheological measurements. Figure 6 shows the typical results of these measurements.

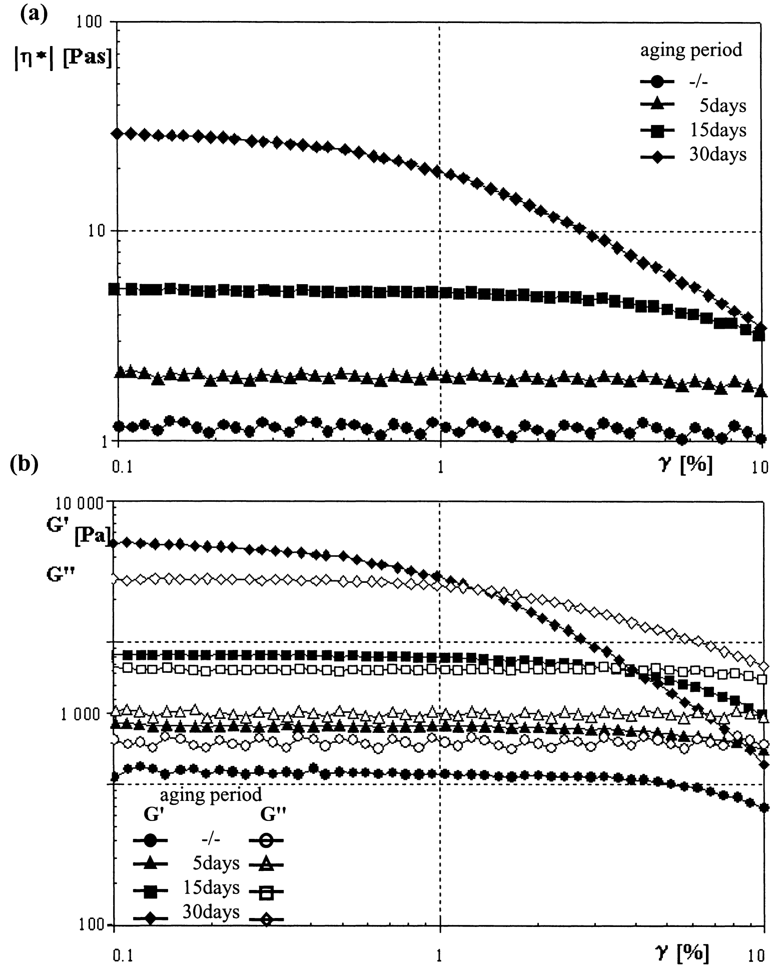

Figure 6. Rheology of resin solutions aged at different times (a) viscosity (η) in dependence of the yield stress (γ). (b) storage modulus (G') and loss modulus (G'') in dependence of the yield stress (γ).

As can be seen by comparing Figure 4 and 6a, concurrent with the formation of larger aggregates a steep increase in viscosity was observed, which reached its final value of more than a factor of 30 above those of the freshly prepared resin. Further the determined storage (G') and loss modulus (G'') clearly indicated the formation of a transient network in aged MF samples, since G`>G`` at low strain and G``>G`at high shear amplitudes (Figure 6b).[13, 6]

This together with the thixotropic behavior of aged MF solutions definitely points towards the presence of a temporary dynamical network clustered by temporary bonds. These are destroyed at high shear amplitudes allowing the aggregates to orient in the flow direction and permitting simultaneously the decrease of viscosity of aged resin solutions.

Concluding Remarks

On summarizing the results of our investigations three main features during the aging process of MF-resins emerge: (a) the formation of micron sized aggregates, whose further aggregation correlates with an increase in viscosity, (b) the formation of a network structure visible by NMR-spectroscopy and rheology and (c) the industrial resins with a solids content of 60% do not indicate crystallization processes as evident by XRD and NMR measurements. We propose that both processes (a) and (b) are responsible for the occurrence of thixotropy by linking together micron sized aggregates generated by phase separation within a noncovalent network (Figure 7). Thus small micron sized droplets form by phase separation of higher molecular weight oligomers from solution and aggregate via noncovalent forces under increase of viscosity. Further experiments for breaking those aggregates are currently under investigations in our research activities.

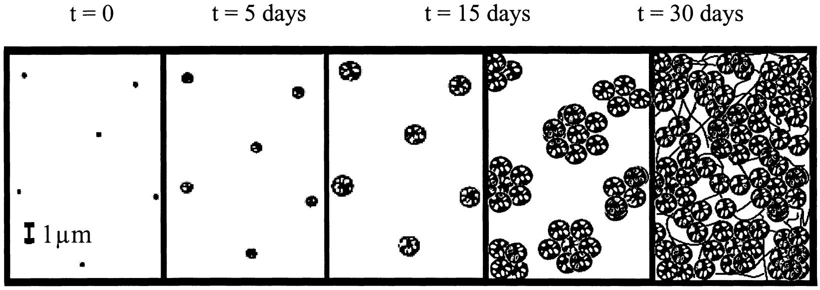

Figure 7. Proposed model of the aging process.

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